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METHOD OF FORMING CEMENTED CARBIDE COATINGS ON METAL SURFACES BY EMPLOYING VOLATILE, ORGANIC LIQUID SOLVENTS AND ORGANIC BINDERS

Ernest R. Ramirez, Zion, Ill., assignor to Howmet Corporation, New York, N.Y., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Cemented carbide coatings and a method for applying the coatings to metal articles. The coating particles primarily comprise a combination of metal carbides and metal binder. The coatings are formed by dipping the articles to be coated at least once into a bath containing the coating particles along with an organic binder in solution with a volatile, organic liquid solvent. The solvent for the bath evaporates during drying while the organic binder is eliminated during sintering. Where more than one coating is formed, smaller amounts of metal binder are employed in the additional coatings. Small amounts of boron and silicon are also added to the coating bath.

This application is a continuation in part of applicant's copending application Ser. No. 401,961, filed Oct. 6, 1964, now abandoned, which is in turn a continuation in part of applications Ser. Nos. 319,967, filed Oct. 30, 1963, now abandoned, and 338,302, filed Jan. 17, 1964, now abandoned.

This invention relates to methods for the coating of metal through the use of powders such as, metal, ceramic and/or metalloid powders. Specifically, the invention is concerned with the production of articles which are provided with such coatings, and the invention is also concerned with the articles produced by the novel methods.

The coating of metals with other metals and with ceramics has long been practiced as a means for providing improved surface properties for the original metal. The improved properties may relate to corrosion resistance, tarnish resistance and abrasion resistance, or they may relate to the aesthetic value of the articles.

In the case of steels, it has been industrial practice to harden the surfaces by carburizing and nitriding processes. Some processes involve coating techniques wherein hardness is imparted to the steel through the addition of a foreign element to the steel surface. The industry has also attempted other methods which would make steel surfaces endure prolonged abrasive action and wear. Thus, hard electrolytic chromium deposits are customarily used to provide rings in internal combustion engines, and such rings have satisfactory hardness as well as excellent wear resistance. Diffusion coatings have also been employed to provide metals with both ceramic and cermet types of coatings. Known techniques include the use of liquid phase sintering to provide such coatings.

It is the general object of this invention to provide a novel method for the formation of a wide variety of coatings on metal surfaces.

It is a more particular object of this invention to provide a disclosure of new techniques specifically concerned with the formation of cemented carbide coatings on metal surfaces.

It is a further object of this invention to establish the conditions which must be met in order that sound, crack-free coatings of cemented carbides can be obtained on steels.

It is a still further object of this invention to provide an improved method for the production of coatings on metallic articles wherein such coatings include ceramic particles alone or in combination with metal and non-metallic particles or compounds.

It is a further object of this invention to provide a method of coating metallic surfaces by a method characterized by its simplicity and high order of efficiency.

These and other objects of this invention will appear below and it will be understood that the specific examples included in this application are provided solely for the purpose of illustration and not by way of limitation.

The concepts of this invention are directed to novel techniques for the application of coatings to metal surfaces. One aspect of this invention relates to the specific method for applying these coatings. This method involves the use of a dip coat bath which is made up of a solvent, an organic binder and the particles which are to be employed for forming the coating. The metal articles to be coated are inserted into the coating bath, and a coating is formed on the article which can thereafter be treated whereby extremely satisfactory adherence can be achieved. The particular formulation of the dip coating bath, particularly the nature of the organic binder employed, and the techniques involved in forming the coatings are primarily responsible for the extreme efficiency of the novel method as well as for the highly satisfactory results obtained.

In the case of carbide coating formation, the compositions of the powders which are first applied to the metal surfaces are of particular importance. Thus, it has been found that satisfactory cemented carbide coatings can only be obtained when the metal binder content of the inorganic portion of the composition applied directly to the metal surface is at or above 14 percent by weight. The remaining portions of this first applied composition are made up of metal carbides and metalloids such as boron or silicon. As noted, certain aspects of this invention provide for the use of organic materials such as waxes in the compositions used for applying the coatings.

The metal binder content of the deposits employed in the carbide forming compositions of this invention can be selected from the group of elements corresponding to those elements in groups VIa and VIII of the Periodic Table. Specifically, metals contemplated in accordance with this invention comprise Cr, Mo, W, U, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt.

The minimum metal binder content of the cermet powder layer (first layer) is placed at 14 weight percent, and it has been found that weight percentages of the metal binder in the deposit much above 50 percent are not encouraged, because the desired hardness and wear properties of the sintered coating are much reduced. It has been found that about 30 weight percent of metal binder in the cermet is an optimum amount for the first layer in the case of a steel substrate.

It is also stressed that there is an advantage in using a plurality of layers (coatings) of cermet powders where the first coat will have a thickness between .001 inch and .020 inch and must also contain at least 14 weight percent metal binder in the inorganic portion of the deposit while subsequent layers may have metal binder percentages less than 14 weight percent. The final coatings are preferably made up only of ceramic particles. The thickness of the subsequent layers can be from .001 inch to .020 inch.

The reason why the first layer of the cermet deposit must contain 14 percent or more of metal binder in the cermet coating is not exactly known; however, this phenomenon is thought to be related to the expansion coefficient of the metal binder and that of the metal base. For example, in the case of steel, it is well known that Co, Ni, Fe and Cr, have lineal coefficients of expansion very similar to steel while WC, TiC and other ceramics have vastly smaller lineal coefficients of expansion. Obviously, where similarity exists, there is greater compatibility between coating and base while significant differences result in cracking and other defects in a coating. It is further thought that the similarity in expansion coefficients permits a diffusion bonding condition at the interface and allows for continuous uniform contraction after sintering (during cooling), thereby providing a coating which is metallurgically sound, uniform and crack-free. It will be appreciated that the coatings do not remain as discrete layers after sintering, and that the composition throughout the ultimate coating will tend to be uniform.

Table I given below clearly shows how the percentage of binder metal in the first layer of a cermet coating strikingly reflects on the physical properties of the coating.

TABLE I.—EFFECT OF METAL BINDER CONTENT ON PHYSICAL PROPERTIES OF CEMENTED CARBIDE COATINGS ON 4340 STEEL

Percent by Weight Composition of Coating (first layer)	Appearance of Sintered Coating*	Wear Properties
95 WC, 5.7 Co, 0.3 B	Coating is badly checked and full of cracks.	Very poor.
90 WC, 9.5 Co, 0.5 B	do	Do.
85 WC, 14.1 Co, 0.9 B	Good, but coating is somewhat cracked; reproducibility of coating is poor.	Fair to poor.
70 WC, 28.5 Co, 1.5 B	Coating is excellent; no visible cracks noted.	Excellent.
60 WC, 38 Co, 2 B	Coating is excellent; no visible cracks.	Good.
40 WC, 57 Co, 3 B	Coating excellent; no visible cracks.	Fair.
20 WC, 76 Co, 4 B	Coating excellent	Fair to poor.

*Coatings were sintered at 2,270° F. for one hour. All coatings are approximately .008 inch thick.

It should be noted from Table I that while the sintered cemented carbide coating appearance is good between metal contents of 14.1 and 76 weight percent, the wear properties are best in the range of 28.5 weight percent binder. It will be understood that the above table only applies to the first layer, and where plural layers are formed, the percent of metal binder in the composite coating can be substantially below 14 percent.

Where carbide coatings are concerned, it is obviously one important aspect of this invention to provide a specific amount of metal binder in the first layer of the cermet, and it is contemplated that the application of this layer can be carried out by one of the already known processes such as electrophoretic deposits, spray techniques, or dip techniques already known to the art. However, it has been found that carbide coatings and coatings in general can best be achieved by a technique generally comprising a process which includes the preparation of a bath containing particles of the material for making up the coating on the metallic article. The bath is made up of a solvent and also includes an organic binder. The article to be coated is immersed in the bath whereby the particles therein collect on the surface of the article. The dipping of the article into the particular bath or into

baths of different compositions may be repeated one or more times until a desired thickness of the coating is provided.

Upon completion of the coating operation, the article is removed from the bath and prepared for fixing of the coating as by sintering. The solvent material making up the bath is preferably of a nature which will volatilize as the article is exposed to the atmosphere following the dip coating. Preferably, the sintering or other fixing operation which completes the coating is carried out after this solvent has evaporated. The binder material is preferably selected whereby it will evaporate during the sintering operation so that the only remaining material on the article consists of the particles which are desired for use as a coating. The binder material is selected from the well-known groups of organic binders which serve to hold the coating particles together on the metal surface so that the sintering operation can be effectively carried out.

The described dip coating process utilizes an organic solvent (benzene, toluene, gasoline, kerosene, trichloroethylene) and an organic binder such as waxes, jells or other organic solids. The dip coating operation is best carried out by suspending the metal, ceramic and/or metalloid particles in an organic solvent containing approximately three weight percent organic binder. Suitable compositions for the dip slurries are:

(a) 45 to 90 parts by weight coating powders
(b) 1 to 15 parts by weight organic binder
(c) balance organic solvent

The ratio of the coating powders to the organic binder is important; however, the amount of solvent employed can vary considerably. The selection of the amount of solvent depends to a large extent on the coating thickness desired. Thus, a more fluid bath will produce a thinner coating while a more viscous bath, including less solvent, will provide a thicker coating. For the formation of carbide coatings, the solvent is advantageously employed in amounts between 10 percent and 25 percent by weight, depending on the thickness desired. In this connection, it will also be noted that the temperature of the bath can also be employed as a means for varying the thickness of a coating. Higher temperatures will produce a more fluid bath and, consequently, thinner coatings.

The article to be coated is dipped into the above solution and as the dipped article is removed from the slurry, the solvent evaporates and the coating powders are bonded together by the organic binder (wax). This organic binder in turn is volatilized during the fixing operation thereby leaving the powders on the dipped surfaces.

The following examples will serve to illustrate the concepts of this invention when applied to specific coatings:

Example I

A first layer, 28½ percent metal binder, was formed on a steel surface. To accomplish this, a steel article was dipped into the following slurry:

WC powder	g	140
Cobalt powder	g	57
Boron powder	g	3
Household wax	g	4
Carnauba wax	g	4
Vaseline	g	1
Benzene	cc	50

The slurry temperature was held at 65° C.

2nd slurry:

WC powder (preferably in the range of 1 micron or less)	g	200
Household wax	g	5
Carnauba wax	g	3
Petroleum jelly	g	1
Toluene	cc	50

The second coating was formed over the first. The coated surfaces were then sintered at 2280° F. for one hour in a hydrogen atmosphere. The total sintered coating thickness was .009 inch and the coating was uniform and crack-free. The coating had a cobalt content of about 15 percent by weight and a boron content of about 0.75 percent by weight.

Example II

TiC powder	g--	130
Nickel powder	g--	60
Chromium powder	g--	10
Boron powder	g--	2
Silicon powder	g--	2
Household wax	g--	4
Carnauba wax	g--	4
Vaseline	g--	1
Kerosene	cc--	50

A steel specimen was dipped into the above slurry held at 60° C. and subsequently vacuum sintered at 2280° F. for one hour. The coating was smooth, uniform and bright and it was .006 inch thick.

Example III

	Gram
TiC	200
Ni	40
Mo	20
Si	5
Wax	5
Carnauba wax	4
Vaseline	1
Toluene	50

The dip was carried out at 65° C. and sintering was effected at 2600° F. in vacuum.

Example IV

Cobalt powder	g--	58
Boron powder	g--	3
Chromium powder	g--	11.6
Tungsten carbide powder	g--	127.4
Carnauba wax	g--	4.5
Petroleum wax	g--	2.5
Petroleum jelly (Vaseline)	g--	1.0
Benzene	cc--	50

A 1020 steel article was introduced into a bath of the above composition, the bath being maintained at a temperature of 60° C. The article was held in the bath for a few seconds, was removed from the bath and allowed to dry.

Thereafter, a second coat was applied employing a bath of the same composition of organic binders and solvents but including 54 grams cobalt, 6 grams silicon, 10.8 grams chromium and 129.2 grams tunsten carbide. Finally, a third coat was applied employing a bath containing the same amounts of organic binders and solvents but employing 200 grams of tungsten carbide as the coating powders.

The article carrying the composite coating was dried for about 12 hours. Thereafter, the article was subjected to a sintering operation at a temperature of 2280° F. for about 30 minutes. The ultimate coating was about .007 inches thick, with the total thickness being provided in equal parts in each of the dip coating steps.

As set forth in copending application Ser. No. 319,967, now abandoned, the instant invention also involves coating of metal articles with a wide variety of materials other than the combinations of carbide and metal binders. Thus, metal oxides can be provided alone or in combination with other materials including elemental metals. The elemental metals can be provided as coatings by means of the described techniques and materials such as graphite are also contemplated for use. It will be understood that wide varieties of organic and inorganic compositions, which can be provided in powder form in dip coating baths of the type described, are susceptible of use in accordance with the principles described herein.

The instant invention is not limited to the coating of steel articles. Specifically, it is contemplated that cobalt and nickel base articles, as well as a wide variety of other alloying compositions, can be treated in accordance with the inventive concepts. Insofar as steel is concerned, high speed steel and stainless steel as well as various alloy and carbon steels are obviously contemplated.

With reference to the procedures of this invention involving dip coating, it will be understood that the powders employed in providing the coating bath are suspended in the solvent. The solvent is selected from a group of well-known volatile solvents which preferably dissolve the organic binder employed in combination therewith. It will be apparent from the character of the solvents referred to above that other similar materials well-known to those skilled in the art could be employed for the stated purposes.

Suitable binders comprise a well-known group of organic binders which are preferably chosen so that they will be removed during the operations required for adhering the coating powders to the metal surface. It is contemplated, however, that the binders or remnants thereof could remain particularly if the fixing operation does not involve high temperatures.

In the case of metal, ceramic and cermet powders, the organic binders are chosen so that they will be removed at least through burn-off during the sintering operation to thereby leave uncontaminated the materials which make up the adherent coating. The binders which are employed serve to hold the powder particles together after the volatile solvent has evaporated upon removal of the article from the coating bath. It will be apparent that if the binder is dissolved in the solvent, then it will come out of solution upon evaporation of the solvent. Suitable binders may be selected from the wide group of waxes and resins commonly employed as binder materials including the following: beeswax, candelilla, carnauba, ceresine, exparto, paraffin or household wax, Japan wax, curicury, ozokerite, spermacetic, sugar cane wax, petroleum jelly. Polyethylene and camphor also comprise suitable materials for these purposes. It will be apparent from considering the above examples that combinations of these binders are advantageously employed for use in accordance with this invention.

With respect to the sintering operation which is carried out, it is preferred that this operation be conducted at temperatures between 2275° F. and 2325° F. although in some cases, other temperatures between 2200° F. and 2600° F. can be employed. The sintering can be characterized as liquid phase sintering, and a metallurgically sound cermet layer on steel and other metals, which is free from cracks and other defects can be produced by the techniques of this invention. The temperature limits are, of course, governed by the melting point of the metal being coated.

In considering the above examples, it will be noted that in the formation of carbide coatings, boron and/or silicon additions are provided. The provision of these elements is an extremely important factor insofar as the carbide coatings are concerned. The instant invention is not to be limited by any theory of operation; however, it is believed that these additions are particularly important insofar as the achievement of an extremely adherent coating is concerned. In the case of boron, there is an improvement in fluidity during sintering with the wetting action of the coating relative to the case metal being improved. This is believed to provide ideal conditions for achieving an adherent bond. The silicon acts in a similar manner although the boron is more suitable as far as the initial dip coat is concerned.

It has been found that boron additions can be employed in amounts between .02 and 1.0 percent by weight of the ultimate composite coating. The silicon is added

in amounts between .15 and 7.5 percent by weight of the ultimate coating. Where combinations of these elements are utilized, then the above ranges should be applied to the particular coating in which the particular element is added.

The use of more than one element for forming the metal binder also provides certain advantages. In the groups of metals described as suitable for use as metal binders, it is contemplated that any one of these metals could be employed in combination.

The combination of cobalt and chromium as set forth in Example IV is extremely satisfactory where carbide coatings are to be formed. The chromium forms an eutectic with cobalt to provide a lower melting point in the coating, thereby providing more satisfactory conditions for sintering whereby a more adherent bond can be accomplished. The combination is particularly suitable where boron is involved since the ternary eutectic which is provided presents ideal conditions. In addition, the chromium is important since it provides an improvement in fluidity during the sintering operation. The chromium is preferably employed in an amount between 0.5 and 4.5 percent by weight of the ultimate coating. In a chromium-cobalt combination, the chromium-cobalt ratio is preferably between 0.1 and 0.4 to 1.

It will be obvious when considering the above disclosure that unique carbide coatings and means for their formation have been described. Furthermore, the techniques for forming the carbide coatings are applicable to the coating of a wide variety of materials on various metal bases. This technique involves the use of novel bath compositions and a novel approach for applying the coatings. The particular bath composition and the provision of the method for coating in the composite fashion described provides many obvious advantages over techniques presently employed for the formation of adherent coatings.

Particularly where carbide coatings are concerned, it is preferred that the average amount of metal binder in the ultimate composite coatings be between 40 and 6 percent and preferably between 33 and 9 percent by weight of the coating composition. It will be understood, however, that the upper limit is a practical limit only since higher percentages of binder are clearly possible but produce an unduly soft coating.

The metal carbides which are included along with the metal binder in the ultimate coating may comprise any one of any combination of carbides known and used by the art. Carbides including chromium, tungsten, titanium, tantalum, columbium and vanadium comprise some of the more well-known compounds of this class. The metal binders utilized therewith are included alone or in various combinations with any of these well-known carbides.

That which is claimed is:

1. In a method for providing a cemented carbide coating on a metal article selected from the group consisting of iron, cobalt and nickel base articles, wherein a coating is applied to the article and the article is then sintered to provide for adherence of the coating thereto, the improvement comprising the steps of preparing a dip coating bath including a volatile, organic liquid solvent, an organic binder in solution with said solvent, and inorganic coating particles, said inorganic particles consisting essentially of metallic carbide consisting of at least one member selected from the group consisting of chromium, tungsten, titanium, tantalum, columbium, and vanadium carbides, and at least 14 percent by weight metal binder based on the total weight of said inorganic particles, the metal binder being selected from the group of metals in groups VIa and VIII of the Periodic Table and combinations thereof, said bath comprising between 45 and 90 percent by weight of coating particles and from one to 15 percent by weight organic binder with the balance comprising said solvent, said solvent being present in an amount sufficient to dissolve the organic binder and in an amount sufficient to provide a fluid bath, immersing said article into said bath to form a first coat including said inorganic particles on said article, removing said article from said bath and forming at least one additional coat over the first, the additional coats containing smaller amounts of metal binder with the total metal binder in the ultimate composite coating comprising between 6 and 40 percent by weight of said ultimate coating, and sintering said article to achieve an adherent ultimate coating composed substantially of said inorganic particles, said solvent and said organic binder being released from said coating after removal of said article from said bath and prior to completion of said sintering operation.

2. A method in accordance with claim 1 wherein said coating is provided in a plurality of applications and wherein the first application immediately adjacent the surface of said article is at least .001 inch in thickness after sintering.

3. A method in accordance with claim 2 wherein said first application comprises about 30 percent by weight of said metal binder.

4. A method in accordance with claim 1 wherein the sintering operation is carried out at a temperature between 2200 and 2600° F.

5. A method in accordance with claim 1 wherein said solvent evaporates upon removal of said article from said bath and wherein said organic binder is released from said coating during said sintering step.

6. A method in accordance with claim 1 wherein said composite coating is formed in three separate coating operations with the final coating being substantially all metal carbide, and wherein the metal binder content is between 9 and 33 percent by weight of the composite coating.

7. A method in accordance with claim 6 wherein at least one of the elements consisting of from .02 to 1.0 percent by weight boron and from .15 to 7.5 percent by weight silicon is included in said composite coating.

8. A method in accordance with claim 7 wherein said metallic carbide comprises tungsten carbide and wherein said metal binder comprises a combination of chromium and cobalt with the chromium-cobalt ratio being between 0.1 and 0.4 to 1.

9. In a method for providing a cemented carbide coating on a metal article selected from the group consisting of iron, cobalt and nickel base articles, wherein a coating is applied to the article and the article is then sintered to provide for adherence of the coating thereto, the improvement comprising the steps of preparing a dip coating bath including a volatile, organic liquid solvent, an organic binder in solution with said solvent, and inorganic coating particles, said inorganic particles consisting essentially of metallic carbide consisting of at least one member selected from the group consisting of chromium, tungsten, titanium, tantalum, columbium, and vanadium carbides, at least 14 percent by weight metal binder based on the total weight of said inorganic particles, the metal binder being selected from the group of metals in groups VIa and VIII of the Periodic Table and combinations thereof, and at least one of the elements consisting of from .02 to 1.0 percent by weight boron and from .15 to 7.5 percent by weight silicon based on the total weight of said inorganic particles, said bath comprising between 45 and 90 percent by weight of coating particles and from one to 15 percent by weight organic binder with the balance comprising said solvent, said solvent being present in an amount sufficient to dissolve the organic binder and in an amount sufficient to provide a fluid bath, immersing said article into said bath at least one time for forming a first coat whereby at least one coating including said inorganic particles is formed on said article, removing said article from said bath and sintering said article to achieve an adherent coating composed substantially of said inorganic particles, said solvent and said organic binder being released from said coating after removal of said ar-

ticle from said bath and prior to completion of said sintering operation.

10. A method in accordance with claim **9** wherein said metallic carbide comprises tungsten carbide and wherein said metal binder comprises a combination of chromium and cobalt with the chromium-cobalt ratio being between 0.1 and 0.4 to 1.

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ALFRED L. LEAVITT, Primary Examiner

J. R. BATTEN, JR., Assistant Examiner

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